Experimental report

19/01/2021

Proposal:	**5-14-273**	**Council:**	10/2019

Title: INFLUENCE OF Fe/Cu CATIONIC ORDER ON THE MAGNETIC GROUND STATE OF YBaCuFeO5 SINGLE-CRYSTALS

Research area: Materials

This proposal is a new proposal

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Samples: YBaCuFeO5 single-crystal

Instrument	Requested days	Allocated days	From	To
D9	10	10	31/08/2020	10/09/2020

Abstract:

YBaCuFeO5 displays magnetism-driven ferroelectricity (FE) at unexpectedly high temperatures. Electrical polarization develops associated to a spiral magnetic order, whose ordering temperature can be increased by more than 150 K (far beyond RT) by manipulating the Cu/Fe chemical disorder in the bipyramids (Nature Comms 7, 13758 (2016)). However, the competition between the spiral and other collinear orders is very poorly understood. In order to shed light on the relevance of some structural features such as the degree of chemical order or the inter- and intra- bowtie separations (d1/d2) (Science Adv. 4, eaau6386 (2018)) for determining the magnetic (and dielectric) ground state, we aim to investigate a high-quality YBCFO single-crystal where -instead of the incommensurate spiral phase- the groundstate has been substituted by commensurate magnetic states with doubled a and b dimensions.

Experimental Report

Title: Influence of Fe/Cu cationic order on the magnetic ground state of $YBaCuFeO_5$ single-crystals
Instrument: D9
Experiment number: 5-14-273
Experimental Team: Arnau ROMAGUERA CAMPS (main proposer), Xiaodong ZHANG, Jose Luis GARCIA-MUÑOZ
Local Contact: Oscar Ramon FABELO ROSA
Date: 31/08/2020 - 10/09/2020

Abstract

YBaCuFeO5 displays magnetism-driven ferroelectricity (FE) at unexpectedly high temperatures. Electrical polarization develops associated to a spiral magnetic order, whose ordering temperature can be increased by more than 150 K (far beyond RT) by manipulating the Cu/Fe chemical disorder in the bipyramids (Nature Comms 7, 13758 (2016)). However, the competition between the spiral and other collinear orders is very poorly understood. In order to shed light on the relevance of some structural features such as the degree of chemical order or the inter- and intra- bowtie separations (d1/d2) (Science Adv. 4, eaau6386 (2018)) for determining the magnetic (and dielectric) ground state, we aim to investigate a high-quality YBCFO single-crystal where -instead of the incommensurate spiral phase the ground state has been substituted by commensurate magnetic states with doubled a and b dimensions.

Report

As outlined in the proposal, the complexity of the Traveling Solvent Floating-Zone (TSFZ) crystal growth technique used to prepare YBaCuFeO5 single crystals makes it elusive to obtain the optimal distribution of Fe/Cu cations in the bipyramids. As a consequence, from the several growth experiments carried out in our lab we obtained crystals where the incommensurate satellites characteristic of the spiral phase, $\mathbf{k}_2$=[1/2,1/2,1/2±δ], have been suppressed and replaced by a new translational symmetry $\mathbf{k}_3$=[1/2,1/2,0], and crystals which resulted in the good conditions for the appearance of the incommensurate (ICOM) magnetic ordering transition (T_S=T_{N2}), with a spiral ordering transition at 195K.

In order to understand the origin of this anomalous behaviour, measurements were done on three different YBCFO single crystal samples: *Sample1* (*YBCFO_xtal7_D*) and *Sample2* (*YBCFO_xtal3_H*), which have the anomalous $\mathbf{k}_3$ commensurate (COM) magnetic order, and *Sample3* (*2002YBCFO_xtal3b*), which has the incommensurate $\mathbf{k}_2$ magnetic order. Previous to the measurements on D9, the three crystals were selected using Orient Express, assessing its homogeneity and orientation (Fig. **1B**). Then, further temperature dependent Laue images were collected on Cyclops (exp. EASY-694) along the 50-300K range with the aim of identifying the magnetic propagation vectors and monitoring its evolution with temperature (Fig. **1C**).

For the measurements, crystals were wrapped in thin aluminium foil to improve its adherence to the dedicated refractory cement. Then, a pin with the glued sample was mounted on the four-circle diffractometer with the corresponding environment: the self-dedicated closed shell furnace was used for the measurements at high temperature, and the displex cryostat was be used to cover the low temperature range. The wavelength during the experiment was λ=0.837Å.

Previous to any measurement, the orientational UB matrix which describes the sample orientation with respect to the diffractometer angles was calculated from several well centered Bragg reflections. Then, nuclear reflections were collected for each crystal at 450K, well above the paramagnetic transition (T_{N1}), achieved using the closed shell furnace. In order to obtain a good structural model that allows us to determine the structural differences in Fe/Cu cationic order and interatomic spacing (d_1 and d_2, shown in Fig. **1A**), which give raise to the different magnetic phases, we have recorded in total 295 Bragg reflections. *DataRED* program is used to read the list of measured reflections and reduce it to a single crystal diffraction pattern consisting of a unique set of independent reflections, which is used to refine the extinction parameters and crystal structure using *FullProf* software (Fig. **1D**). By this method, structural models are obtained at 450K for each crystal.

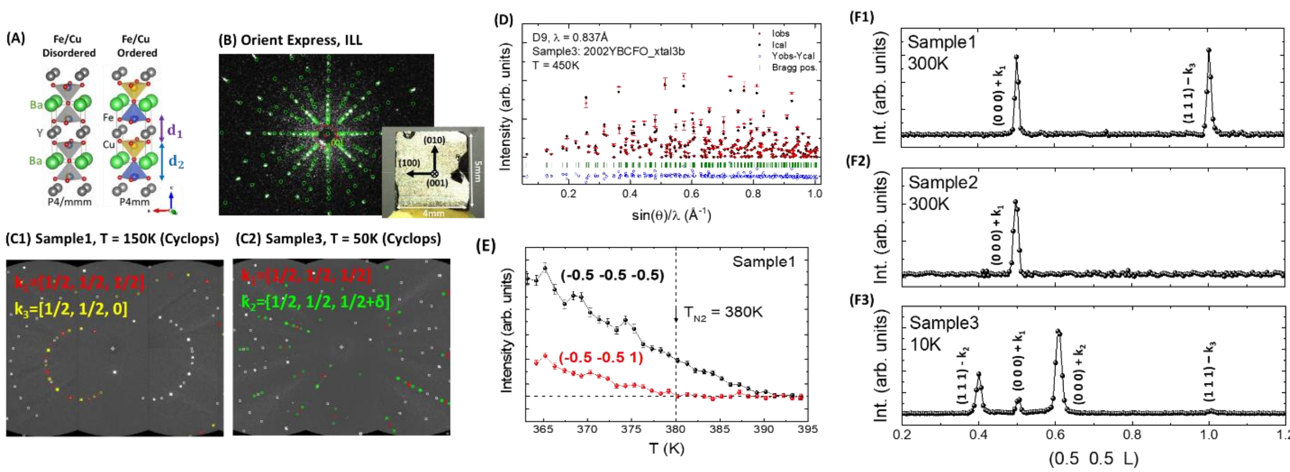

Figure 1. (**A**) Projections of *P4/mmm* and *P4mm* structures; (**B**) Laue diffraction pattern collected on Orient Express showing the *c*-axis of *Sample3* crystal perpendicular to the detector, and an image of the single crystal showing its dimensions and orientation; (**C**) Section of a Laue diffraction pattern collected on Cyclops at 50K showing the indexation of the nuclear reflections (in white) and the magnetic propagation vectors in different colours, for the COM (fig. C1) and ICOM (fig. C2) crystals (Sample1 and Sample3, respectively); (**D**) Rietveld refinement of the integrated single-crystal nuclear reflections, collected at 450K on *Sample3*; (**E**) Evolution of the integrated magnetic intensity of reflections (-1,-1,-1) + $\mathbf{k}_1$ and (-1,-1,1) + $\mathbf{k}_3$ as function of temperature; (**F**) q-scans measured along the (0.5 0.5 L) curve, with L ranging from 0.2 to 1.2 in order to asses the propagation vectors in the different crystals: (fig. F1) *Sample1* shows propagation vectors $\mathbf{k}_1$ and $\mathbf{k}_3$ at 300K, (fig. F2) *Sample2* shows only propagation vector $\mathbf{k}_1$ at 300K, (fig. F3) *Sample3* shows propagation vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ at 10K.

In addition to the nuclear reflections at 450K, further preliminary measurements on magnetic reflections were done for the different crystals. Q-scans have been collected along L keeping constant H=0.5 and K=0.5. The range of the (0.5, 0.5, L) scans goes from L=0.2 to L=1.2 in order to assess the presence of the different propagation vectors in each crystal (Fig. **1F**). It is of special interest the case of *Sample3*, for which we can do so some observations based on the q-scan at 10K: (i) the presence of $\mathbf{k}_3$ magnetic phase is negligible; (ii) the ground magnetic state is the ICOM phase $\mathbf{k}_2$; (iii) although at 10K the magnetic order is mostly incommensurate, some amount of $\mathbf{k}_1$ magnetic phase remains ordered well below the ICOM magnetic transition. The following measurements on magnetic reflections are done:

-On *Sample1* (T_{N1}=380K, T_{N2}=430K), the integrated intensity of magnetic reflections (-0.5, -0.5, -0.5) and (-0.5, -0.5, 1), corresponding to the respective propagation vectors $\mathbf{k}_1$ and $\mathbf{k}_3$, is monitored along the T_{N2} magnetic transition (Fig. **1E**) to determine with precision the ordering temperature of magnetic phase $\mathbf{k}_3$. After this, 382K is the selected temperature where only magnetic phase $\mathbf{k}_1$ is present to perform a scan of 83 magnetic reflections to refine the collinear magnetic structure.

-On *Sample2* (T_{N1}=280K, T_{N2}=420K), similar measurements are done at 300K, where $\mathbf{k}_1$ is the only magnetic phase. As in the previous case, a set of 83 magnetic reflections is measured on $\mathbf{k}_1$ to refine the magnetic structure.

- Finally, the ICOM magnetic phase in *Sample3* (T_{N1}=195K, T_{N2}=460K) was studied in more detail. First, q-scans of the magnetic reflections were done around the (0.5 0.5 0.5) position in the 10-300K range with a step of 5K, showing the collinear ($\mathbf{k}_1$=[1/2, 1/2, 1/2]) and revealing the ICOM ($\mathbf{k}_2$=[1/2, 1/2, 1/2±δ]) magnetic ordering transition at T_S=T_{N2}=195K (Fig. **2B**), the highest T_S reported for an YBCFO crystal. The value of the incommensurability obtained from the q-scans is δ=0.104 Å^{-1} at 10K, which continuously decreases with temperature until it becomes commensurate (Fig. **2C**). In this case 208 magnetic reflections are measured for $\mathbf{k}_2$ at 10K in order to distinguish between distinct incommensurate models (Fig. **2A**).

A smaller set of nuclear reflections is also obtained in all cases to obtain the extinction parameters and atomic displacement factors to complement the refinement of the magnetic phases. In the case of the incommensurate crystal (*Sample3*), a larger set consisting of 295 Bragg reflections is collected at 10K in order to compare with the structure at 450K. Results will be conveniently published.

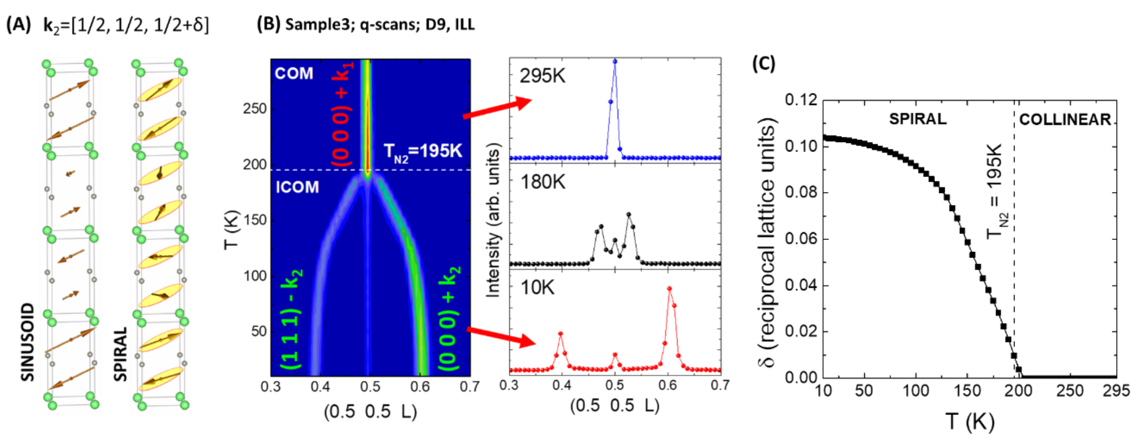

Figure 2. (**A**) Two distinct models for the ICOM magnetic phase of *Sample3*; (**B**) Evolution of the incommensurate q-vector as function of temperature in our YBCFO single-crystal sample with partial Fe/Cu chemical disorder (*Sample3*) around the (0.5 0.5 0.5) position, showing the collinear ($\mathbf{k}_1$) and ICOM ($\mathbf{k}_2$) magnetic phases, measured at the D9 four-circle diffractometer (ILL); (**C**) Evolution of the incommensurability (δ) with temperature for the ICOM propagation vector $\mathbf{k}_2$ =[0.5,0.5,0.5+δ].